(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 May 2001 (17.05.2001)

PCT

(10) International Publication Number
WO 01/34613 A1

(51) International Patent Classification[7]: C07F 7/20, C08G 77/34

(21) International Application Number: PCT/US00/29537

(22) International Filing Date: 26 October 2000 (26.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/438,069 10 November 1999 (10.11.1999) US
09/547,645 12 April 2000 (12.04.2000) US

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(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/34613 A1

(54) Title: PROCESS FOR STABILIZATION OF SILOXANE COMPOUNDS

(57) Abstract: A method for stabilizing silicone dry cleaning solvents containing impurities, comprising contacting the silicone solvent with an adsorbent, neutralizing agent or combination thereof to purify the solvent and prevent reequilibration and polymerization, and separating the silicone solvent.

PROCESS FOR STABILIZATION OF SILOXANE COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of US Serial No. 09/438,069, filed November 10, 1999.

TECHNICAL FIELD

The present invention is directed to a process, more specifically, to a process for stabilizing silicone dry cleaning solvents containing acidic impurities.

BACKGROUND

Current dry cleaning technology uses perchloroethylene ("PERC") or petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments. Volatile siloxanes are being introduced into the dry cleaning industry as an alternative to PERC. However, there exists a need to stabilize the siloxane solvents to prevent undesirable cyclic siloxane (D_4) formation and polymerization.

Methods for the purification of organopolysiloxanes have previously been reported, but they have not been reported for the purification of certain cyclic siloxanes (D_5). Methods for purifying organopolysiloxanes utilizing elemental metals have been reported (see US 5,245,067). Other patents disclose the purification of polyether silicones by contacting with an aqueous acid and removing the odorous materials formed (see US 5,118,764), or the reaction with hydrogen and a hydrogenation catalyst (see US 5,225,509). Hexamethyldisiloxane has been purified by successive treatments with a

condensation catalyst, washing with water, separating the phases, distilling the siloxane, treating with acid clay and then treating with activated carbon (see US 4,774,346). Siloxanes have also been purified by contacting with steam and distilling out the impurities (see EP 543 665). A deodorization method utilizing active carbon to which a functional group has been fixed through a silanol bond has been reported (see US 5,238,899). Finally, a method was reported for purifying silicone oil by adding a drying agent and an adsorption agent to silicone and passing a low water vapor inert gas through the system (see US 4,661,612).

There is a need for stabilizing the siloxane and suppressing reequilibration and polymerization of the volatile siloxane containing acidic impurities that is used in dry cleaning applications.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a method for stabilizing silicone dry cleaning solvents that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation, comprising contacting the silicone solvent with an adsorbent, neutralizing agent, or combination thereof, and separating the silicone solvent.

The process of the present invention is effective in preventing formation of certain cyclic siloxanes (i.e., D_4) that are undesirable in the silicone solvent.

As used herein, the terms "D_4", "D_5" and "D_6" refer to cyclic siloxanes having the formula: $-(R_2SiO)_x-$ where x is 4, 5 or 6 (i.e., D_5 is decamethylcyclopentasiloxane).

DETAILED DESCRIPTION OF THE INVENTION

Preferably, the first preferred embodiment of the method of the present invention comprises, contacting a silicone dry cleaning solvent that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation with an adsorbent, neutralizing agent, or combination thereof, and separating the silicone solvent. Preferably, the silicone dry cleaning solvent is a volatile linear, branched, cyclic or a combination thereof, siloxane.

The amount of these impurities that may be present in the siloxane solvent without preventing reequilibration may be up to about 0.1 parts by weight. The impurities may be introduced into the silicone solvents during the dry cleaning operation, and if they are not removed, reequilibration and polymerization of the solvent may take place, and undesirable cyclics are formed.

Compounds suitable as the adsorbent are those that effectively remove the acidic impurity and prevent gelling and formation of undesirable cyclics in the siloxane solvent. Examples of adsorbents suitable for use include, but are not limited to, carbon black, silica gel, celite, fullers earth, decolorizing charcoal, filtrol, molecular sieves, diatomaceous earth, magnesium sulfate, cob powder, clays, and alumina. In a preferred embodiment, the adsorbent is a selected from silica gel, diatomaceous earth, fullers earth, acid clay, 4A molecular sieves, 13X molecular sieves, and decolorizing charcoal.

Compounds suitable as the linear or branched, volatile siloxane solvent of the present invention are those containing a polysiloxane structure that includes from 2 to 20 silicon atoms. Preferably, the linear or branched, volatile siloxanes are relatively volatile materials, having, for example, a boiling of below about 300°C point at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more compounds of the structural formula (I):

$$M_{2+y+2z}D_xT_yQ_z \qquad \text{(I)}$$

wherein:

M is $R^1{}_3SiO_{1/2}$;

D is $R^2{}_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

and Q is $SiO_{4/2}$

R^1, R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl, monovalent aryl radicals, such as, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl, and monovalent aralkyl radicals such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenyoxypropyl, biphenyloxypropyl.

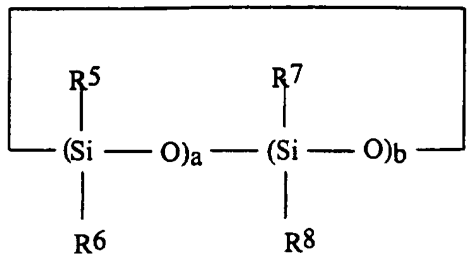
In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent alkyl radical containing from 1 to 6 carbons per group, most preferably, methyl.

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more of, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane or hexadecamethylheptasiloxane or methyltris(trimethylsiloxy)silane. In a more highly preferred embodiment, the linear or branched, volatile siloxane of the present invention comprises octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane. In a highly preferred embodiment, the siloxane component of the composition of the present invention consists essentially of decamethyltetrasiloxane.

Suitable linear or branched volatile siloxanes are made by known methods, such as, for example, hydrolysis and condensation of one or more of tetrachlorosilane, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or by isolation of the desired fraction of an equilibrate mixture of hexamethyldisiloxane and octamethylcyclotetrasiloxane or the like and are commercially available.

Compounds suitable as the cyclic siloxane component of the present invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the linear, volatile siloxanes and cyclic siloxanes are relatively volatile materials, having, for example, a boiling point of below about 300°C at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the cyclic siloxane component comprises one or more compounds of the structural formula (II):



(II)

wherein:

R^5, R^6, R^7 and R^8 are each independently a monovalent hydrocarbon group; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

In a preferred embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of dimethyldichlorosilane and are commercially available.

It is believed that those dry cleaning solvents useful in the present invention that lack a cyclic siloxane component would be more stable than those which include a cyclic siloxane component, in that cyclic siloxanes are known to ring open and polymerize under acidic and basic conditions.

In a first embodiment of the method of the present invention, approximately 100 parts by weight ("pbw") of siloxane solvent that mya can up to 0.1, preferably up to 0.01, even more preferably up to 0.001 pbw of an acidic impurity, contacts up to about 100, more preferably up to about 50, even more preferably up to about 10 pbw of adsorbent, neutralizing agent or a combination thereof, for about 0.0025 to about 6 hours, more preferably for about 0.01 to about 2 hours, even more preferably for about 0.1 to about 0.5 hours, at a temperature of from about 10 to about 80°C, more preferably from about 20 to about 60°C. After the siloxane solvent has contacted the adsorbent for the appropriate time and has been purified, the siloxane solvent can be recycled in the dry cleaning apparatus. The method of the present invention effectively reduces the level of impurities in the silicone solvent.

In a second embodiment of the method of the present invention, a dry cleaning fluid is treated by the method of the present invention.

The method of the present invention also comprises a dry cleaning process comprising the steps of: contacting an article with a silicone solvent, and removing the silicone solvent, then treating the silicone solvent that has been removed by contacting the silicone solvent with an adsorbent, neutralizing agent, or combination thereof, and separating the silicone solvent form the adsorbent, then reusing the treated silicone solvent in the dry cleaning process.

The following examples illustrate the process of the present invention. They are illustrative and the claims are not to be construed as limited to the examples.

EXAMPLE 1

Decamethylcyclopentasiloxane (D_5) that was used as a dry cleaning solvent was mixed with an acid (LPNC) to make a stock solution containing 200 parts per million ("ppm") LPNC. Aliquots of the stock solution were heated to 100°C to determine if the mixture would undergo reequilibration and polymerization (increased D_4 and D_6 levels as well as increased viscosity). The results of the control experiments are shown in Table 1 below. Without any added acid, the D_5 was stable at 100°C for 24 hours. In the presence of 200 ppm LPNC, the viscosity rapidly increased over 7 hours and the composition was unable to be determined.

Absorbents used in Examples

Adsorbent	Type of Adsorbent
A	Diatomaceous earth (Celite® 545)
B	4A molecular sieves
C	Powdered 13X molecular sieves
D	13X molecular sieves
E	silica gel 60-200 mesh
F	acid clay (Filtrol® F-25)
G	fullers earth
H	Powdered decolorizing charcoal (Norit®)

Acids used in Examples

Acid	Type of Acid
T	DDBSA (dodecylbenzenesulfonic acid)
U	LPNC (linear phosphonitrilic chloride)
V	Hydrochloric acid
W	p-Toluenesulfonic acid
X	Acetic Acid
Y	Phosphoric acid
Z	Sulfuric acid

Table 1 - Polymerization and Reequilibration of D_5 with LPNC

Exp #	Temp. (°C)	LPNC (ppm)	Rxn Time (h)	% D_4	% D_5	% D_6	Rxn Time (h)	% D_4	% D_5	% D_6	Visc. Increase
Control	100	None	0	<0.2	99.46	0.47	24	<0.2	99.46	0.47	No
1	100	200	7	-	-	-	24	-	-	-	Gel*

*Viscosity was too high to measure.

EXAMPLE 2

Stock solutions containing 200 ppm acid (LPNC) in D_5 were prepared and then treated with a variety of adsorbents and neutralizing agents. Approximately 0.1 gram of adsorbent was added to 10 grams of solution (1 % loading) and shaken for 1 minute, and then the adsorbent was removed. The solution was heated to 100°C for 4 hours and cyclic levels were measured. Heat was continued until 24 hours, and cyclic levels were again measured. Table 2 shows the results of cyclic formation.

Table 2 - 1% Adsorbent with 1 minute contact time.

Exp. #	Adsorb.	Rxn time (h)	% D_4	% D_5	% D_6	Rxn time (h)	% D_4	% D_5	% D_6
2	H	4	<0.1	99.45	0.54	24	<0.1	99.45	0.55
3	E	4	<0.1	99.45	0.55	24	<0.1	99.45	0.55
4	C	4	<0.1	99.44	0.56	24	<0.1	99.46	0.54
5	I	4	<0.1	99.45	0.55	24	<0.1	99.35	0.55
6	F	2	<0.1	99.46	0.54	24	<0.1	99.43	0.58

Table 2 indicates that using a low loading (1%) and short contact time (1 minute), silica gel, carbon black, fullers earth, powdered 13X molecular sieves and acid clays all effectively prevented polymerization from occurring when compared to the control sample treated with the same level of acid.

EXAMPLE 3

Tables 3 and 4 show the type of acid and the effect of acid level loading on the equilibration of D_5.

Table 3 - 1000 ppm acid in D_5 at 120 °C

Exp. #	Acid	Rxn time (h)	% D_4	% D_5	% D_6	Rxn time (h)	% D_4	% D_5	% D_6
7	V	4	<0.1	99.52	0.48	24	<0.1	99.39	0.61
8	W	4	0.56	99.84	0.59	24	1.93	97.2	1.05
9	X	4	<0.1	99.51	0.49	24	<0.1	99.52	0.48
10	T	4	10.89	80.53	6.27	24	15.12	74	7.67

Table 4 - 1000 ppm acid in D_5

(at 120 °C after treatment with 1% adsorbent for 1 minute)

Exp. #	Adsorbent	Acid	Rxn time (h)	% D_4	% D_5	% D_6	Rxn time (h)	% D_4	% D_5	% D_6
11	None	W	4	0.70	98.31	0.96	24	1.25	98.37	1.14
12	H	W	4	0	99.26	0.74	24	0	99.32	0.68
13	F	W	4	0	99.33	0.67	24	0	99.05	0.95
14	D	W	4	0	99.25	0.75	24	0	99.55	0.45
15	None	T	4	1.08	90.89	3.28	24	2.96	93.05	2.05
16	H	T	4	0	99.26	0.74	24	0	99.30	0.70
17	F	T	4	0	99.23	0.76	24	0	99.26	0.74
18	D	T	4	0	100	0	24	0.04	98.52	1.47
19	None	U	4	Gel	Gel	Gel	24	Gel	Gel	Gel
20	H	U	4	0	99.33	0.66	24	0	99.22	0.78
21	F	U	4	0	99.32	0.68	24	0	99.24	0.76
22	D	U	4	0.73	97.03	0.92	24	0.67	97.92	0.92

For a number of the acids, a high loading was necessary to see reaction with D_5 at elevated temperatures. The same experiments and controls were run with a linear siloxane (MD_2M) containing acids. Results are shown in Tables 5 to 7.

Table 5 - 80 ppm acid in MD_2M at 100 °C.

Exp. #	Acid	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M
23	Control	4	0	0	99.9	0	24	0	0	99.9	0
24	U	4	17.08	18.58	16.11	12.8	24	7.74	6.69	11.57	13.1
25	V	4	0	0	99.9	0	24	0	0	99.9	0
26	W	4	0	0	99.9	0	24	0	0	99.9	0
27	X	4	0	0	99.9	0	24	0	0	99.9	0
28	Y	4	0	0	99.9	0	24	0	0	99.9	0
29	Z	4	0	0	99.9	0	24	0	0	99.9	0

Table 6 - 1000 ppm acid in MD_2M at 120°C.

Exp. #	Acid	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M
30	T	4	11.16	15.02	41.45	12.46	24	13.44	16.52	36.11	13.5
31	W	4	0	0	99.9	0	24	1.3	.82	97.03	.44

Again, high levels of acids were necessary to catalyze the redistribution of MD_2M.

The acid contaminants could be rendered inactive or less active by treatment with numerous agents as shown in Table 7.

Table 7 - 1% Adsorbent with 1 min contact at 200 ppm LPNC in MD_2M at 100°C

Exp. #	Adsorbent	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M	Rxn time (h)	% MM	% MDM	% MD_2M	% MD_3M
32	H	4	<0.1	0	99.01	.89	24	0	0	98.37	1.63
33	E	4	<0.1	0	99.47	.43	24	1.5	.72	96.12	.7
34	C	4	<0.1	0	99.57	.33	24	0	0	98.03	.29
35	D	4	20.51	21.7	17.65	13.74	24	12.98	19.28	17.74	15.3
36	B	4	10.28	15.49	19.27	16.66	24	21.75	22	17.74	13.68
37	G	4	<0.1	0	98.90	0	24	0	0	98.9	0
38	F	4	<0.1	0	99.60	.296	24	0	0	99.22	0
39	A	4	21.33	21.49	17.65	13.94	24	15.21	18.64	15.74	12.58

The process of the present invention is effective in reducing the level of acidic impurities in the silicone solvent.

CLAIMS:

1. A method for stabilizing silicone dry cleaning solvents that may contain an undesirable acidic impurity capable of causing cyclic siloxane formation comprising, contacting the silicone dry cleaning solvent with an adsorbent, neutralizing agent, or combination thereof, and separating the silicone solvent from the adsorbent.

2. The method of claim 1, wherein the amount of adsorbent, neutralizing agent, or combination thereof used is up to 100 parts by weight per 100 parts by weight of silicone solvent.

3. The method of claim 1, wherein the solvent contacts the adsorbent, neutralizing agent or combination thereof for about 0.0025 to about 6 hours.

4. The method of claim 1, wherein the solvent contacts the adsorbent, neutralizing agent or combination thereof at a temperature of from about 10 to about 80°C.

5. The method of claim 1, wherein the adsorbent used is selected from the group consisting of silica gel, diatomaceous earth, fullers earth, acid clay, 4A molecular sieves, 13X molecular sieves, and decolorizing charcoal.

6. The method of claim 1, wherein the solvent is a linear or branched siloxane comprising one or more compounds of the structural formula:

$$M_{2+y+2z}D_xT_yQ_z$$

wherein:

M is $R^1{}_3SiO_{1/2}$;

D is $R^2{}_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

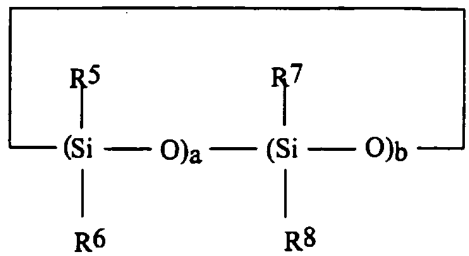
and Q is $SiO_{4/2}$

R^1, R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

7. The method of claim 6, wherein the linear or branched, volatile siloxane of the present invention comprises octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane.

8. The method of claim 1, wherein the silicone is a cyclic siloxane comprising one or more compounds of the structural formula:



(II)

wherein:

R^5, R^6, R^7 and R^8 are each independently a monovalent hydrocarbon group; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

9. The method of claim 8, wherein the cyclic siloxane is octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane.

10. The method of claim 1, wherein the acidic impurities removed from the solvent are linear phophonitrilic chloride, sulfuric acid, hydrochloric acid, methanesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, acetic acid, sulfuric acid or sulfuric acid or a combination thereof.

11. A silicone dry cleaning fluid treated by the method of claim 1.

12. An adsorbent used in the method of claim 1, wherein the adsorbent comprises the impurities removed from the solvent are linear phophonitrilic chloride, sulfuric acid, hydrochloric acid, methanesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid, acetic acid, sulfuric acid or sulfuric acid or a combination thereof.

13. A dry cleaning process comprising:

(a) contacting the article with a silicone solvent; and

(b) removing the silicone solvent; and

(c) contacting the removed silicone solvent with an adsorbent, neutralizing agent, or combination thereof; and

(d) separating the silicone solvent from the adsorbent.

14. The process of claim 13, further comprising reusing the treated silicone solvent in step (1).

15. The process of claim 13, wherein the adsorbent used is selected from the group consisting of silica gel, diatomaceous earth, fullers earth, acid clay, 4A molecular sieves, 13X molecular sieves, and decolorizing charcoal.

16. The process of claim 13, wherein the dry cleaning process comprises a plurality of dry cleaning cycles comprising steps (a) and (b), and a plurality of stabilizing cycles comprising steps (c) and (d), wherein the dry cleaning cycle is repeated one or more times per each stabilizing cycle.

INTERNATIONAL SEARCH REPORT

Int :ional Application No
PCT/US 00/29537

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F7/20 C08G77/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 186 736 A (LICENTIA GMBH) 9 July 1986 (1986-07-09) cited in the application claims 1-11	1-10,12
X	DE 29 04 706 A (GEN ELECTRIC) 30 August 1979 (1979-08-30) page 15 -page 16 claim 1	1-10,12
X	US 3 755 152 A (GULICK G) 28 August 1973 (1973-08-28) column 2 -column 8; claims 1-9; examples 1-11	1-10,12
A	DE 37 39 711 A (KREUSSLER CHEM FAB) 8 June 1989 (1989-06-08) page 3 -page 4; examples 1-3	1,11,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int· ·ional Application No
PCT/US 00/29537

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